

The Effect of Boron Compound to Cement Hydration and Controllability of this Effect

M. DAVRAZ*

Suleyman Demirel University, Natural and Industrial Building Materials Application and Research Center, Isparta, Turkey

The use of boron compounds as composites of cementitious, except for the limited usage conditions like setting retarder has not become widespread because of the hardening and the related problems. In this study, the effects of the boron compounds into hydration process of the different cement types and controllability of these effects was investigated. Portland cement, boron modified active belite cement, and calcium aluminate cement were used in the mortar mixtures as binder material. Except for the control mixture, boric acid (BA) was used at the ratios of 0.25–1.00% of weight of cement in mortar mixtures with Portland cement. Setting times dependent on pH, EC and T changes of fresh mortars were measured. With increasing BA concentration, setting times of the mortars rather increased, pH, electrical conductivity, and T values of the mortars significantly reduced. To suppress the affect of BA on the hydration process, the two various stabilizers were used in the mortars, setting times, pH, electrical conductivity, and T values of these mortars were measured again. As a result, the optimum workability times and the parameters of the hydration reaction taking into account, the most suitable type and usage ratio of stabilizer were determined for mortars with BA.

DOI: [10.12693/APhysPolA.128.B-26](https://doi.org/10.12693/APhysPolA.128.B-26)

PACS: 81.05.Mh

1. Introduction

Boron compounds (BC) such as boric acid ($B[OH]_3$) and borates extend the period of cement hydration. Therefore, BCs are used in concrete as an efficient set retarding admixture, such as hydroxylated carboxylic acid, lignins, sugar and some phosphate compounds. Borates have been used regularly in oil-well cementing operations both as a conventional retarder and also an auxiliary admixture for viscosity at high temperatures [1]. Furthermore, radioactive wastes of nuclear power plants is mixed with high borate concentration solutions and then this mixture is solidified using cement to store in underground. However, during the hardening process, major strength problems have not been resolved yet. Excluding these two specific conditions of use, the use of BC with inorganic binders could be become widespread so far because of hardening and the related strength problems.

In recent years, many researches have been carried out for the usability of boron wastes on cement production. Kula et al. have stated that the use of tincal ore waste also gives rise to an improvement in the properties of the Portland cement (PC) at 1% replacement level. Although it retards setting time (ST), it gives an opportunity for use as a cement replacement material up to 5 wt% of the cement [2].

According to Targan et al., the compressive strength of concrete specimens made by cement with grinding the 81–96% Portland clinker, 4% colemanite waste and 5–15% natural pozzolan materials at 90 days of curing

performs 90% of control concrete specimens [3]. In 2006 year, GOLTAS Cement Factory in Turkey has produced boron modified active belite cement (BAB) with using colemanite ore. In researches on this cement type, it is stated that this product could be successfully used specially in dam concretes due to its very low hydration temperature (HT) with no alite phase.

In addition, the final compressive strength of concrete made by BAB cement is much higher than that of concrete's made by PC [4]. In appropriate concentrations, properties such as shrinkage and fire resistibility of concrete and other cementitious composites including BCs may be improved. Furthermore, these products may also gain new features such as radiation impermeability and antibacteriability. In some researches, studied on this subject, Volkman et al. (1992) have stated that as adding the BCs to concrete, they absorb the neutrons and low energy gamma rays spread. Therefore, there could be supplied an effective radiation protection.

However, adding boron compound to concrete mix seriously retards the ST and decreases the concrete strength [5].

On the other hand, Demir et al. [6] have prepared the concrete specimens including borogypsum and colemanite concentrator wastes. They tested the differences in gamma rays passing energies for normal and boron waste (BW) additive concretes specimens. They observed that concrete specimens including BW supply an effective protection against radioactive radiations.

BOREN stated that BAB cement has more than 20% of a neutron absorbing capacity comparing to PC [7]. The improvements and additional features provided BCs to concrete and cementitious composites are very closely relevant to B_2O_3 concentrations of using BCs.

*e-mail: metindavraz@sdu.edu.tr

Furthermore, increasing the B_2O_3 concentration slows down the cement hydration and even stops it. Extending the ST depending on that situation is known and an intensively research phenomenon.

In Taylor paper [8] borates are mentioned very briefly as being compounds that generally retard cement hydration, possibly by a precipitation mechanism.

In Conner work [9] borates are listed as short-term setting retarders that disrupt the cement matrix.

Jeffrey et al. [10] found that it was difficult to stabilize any liquid BW waste having a concentration of dissolved boron of more than 12% using cement and extra lime for pH control.

As adding BC into mortar mixture, boron trioxide (B_2O_3) concentration is one of the most important factors affecting the quality of cementitious composites (fire resistant, neutron shield etc.). In priority, beneficial B_2O_3 concentration should be determined depending on the aim. The concentration depends on the B_2O_3 % of compound including. As the B_2O_3 concentration decreases ($< 0.20\%$), the hardening retard and the strength decreases will improve linearly as well. However, physical and chemical benefits of B_2O_3 to cement composite

will decrease. Forming calcium diborate (CBH_6) barrier layers on grain surfaces should be delayed to reach to optimum ST and the strength value in relevant B_2O_3 concentration. Thus, effects on cement hydration of both the direct and indirect using method of B_2O_3 were researched in this study. For this purpose, the effect of combined use of $B[OH]_3$ as a B_2O_3 source and accelerator additive materials on mortar set time and cement hydration was also investigated in this study.

2. Material and methods

BA obtained from Eti Mine as a source of B_2O_3 , PC and BAB obtained from GOLTAS and calcium aluminate cement (CAC) obtained from CIMSA were used in this study. Also accelerator additive materials such as calcium chloride (CC), sodium aluminate (SA) were added in the mortar mixtures in order to suppress the retarding affect of BA to cement hydration. The dosages of cement used in all specimens are equal. Physical and chemical properties of PC, BAB and CAC cements used as a binder were given in Table I.

TABLE I

Physical and chemical properties of cements used as a binder [11, 12].

Chemical prop. of clinkers				Physical prop. of cements			
Components [%]				OPC	BAB	CAC	
SiO ₂	20.52	20.37	2.20	volumetric expansion [mm]	1	0	0
Al ₂ O ₃	4.00	4.45	40.70	fineness [90 μm]	0.1	0.1	6.5
Fe ₂ O ₃	3.45	3.27	17.00	slightness [200 μm]	1.1	1.8	1.2
CaO	64.28	58.19	38.20	specific surface area [cm ² /g]	3340	3560	3540
MgO	1.63	4.70	0.80	initial setting time [min]	185	220	245
SO ₃	2.53	3.08	0.02	final setting time [min]	240	265	265
Na ₂ O+K ₂ O	1.35	1.50	0.07	specific gravity [g/cm ³]	3.12	2.98	3.29
B ₂ O ₃	0.00	1.12	0.00	flexural strength [MPa, at 2 days]	4.5	2.5	6.0 ^a
CaO (free)	1.81	0.63	–	flexural strength [MPa, at 7 days]	5.8	4.1	7.5 ^b
L.O.I.	2.72	4.02	0.30	flexural strength [MPa, at 2 days]	7.2	6.0	9.5 ^c
Clinker phases [%]				compressive strength [MPa, at 2 days]	11.7	11.7	55.2 ^d
C ₃ S	–	56.66		compressive strength [MPa, at 7 days]	39.3	23.2	81.6
C ₂ S	66.23	17.65		compressive strength [MPa, at 28 days]	51.0	38.6	–
C ₃ A	7.86	6.33		Other prop. of cements			
C ₄ AF	14.01	12.03		Cl ⁻	0.000	0.006	0.000

^a6 h, ^b24 h, ^c6 h, ^d24 h

In cement-compounds in order to reach the optimal ST and strength value in an appropriate concentration of the B_2O_3 it is needed to prevent the formation of barrier layers on the surface of cement grains or at least delay this. In this study at first chemical additive types that can prevent the retardation of ST in different cementitious compounds having B_2O_3 concentration and

with the aim of determining usage ratios, 35 different mortar specimens were prepared as two for each (Table II). Each mortar specimen prepared, primarily initial setting times (IST) and final setting times (FST) were measured with automatic Vicat apparatus as appropriate to TS EN 196-3 standards [13].

TABLE II

The components of mortar specimens.

Mix code	CEM	BA [%]	AC [%]		Mix code	CEM	BA [%]	AC [%]	
PC	PC	0	N	0	0.75BA+PC+1.5SA	PC	0.75	SA	1.5
BAB	BAB	0	N	0	1.00BA+PC+1.5SA	PC	1.00	SA	1.5
CAC	CA	0	N	0	0.25BA+PC+2.0SA	PC	0.25	SA	2.0
0.25BA+PC	PC	0.25	N	0	0.50BA+PC+2.0SA	PC	0.50	SA	2.0
0.50BA+PC	PC	0.50	N	0	0.75BA+PC+2.0SA	PC	0.75	SA	2.0
0.75BA+PC	PC	0.75	N	0	1.00BA+PC+2.0SA	PC	1.00	SA	2.0
1.00BA+PC	PC	1.00	N	0	0.25BA+PC+1.0CC	PC	0.25	CC	1.0
0.25BA+CAC	CA	0.25	N	0	0.50BA+PC+1.0CC	PC	0.50	CC	1.0
0.50BA+CAC	CA	0.50	N	0	0.75BA+PC+1.0CC	PC	0.75	CC	1.0
0.75BA+CAC	CA	0.75	N	0	1.00BA+PC+1.0CC	PC	1.00	CC	1.0
1.00BA+CAC	CA	1.00	N	0	0.25BA+PC+1.5CC	PC	0.25	CC	1.5
0.25BA+PC+1.0SA	PC	0.25	SA	1.0	0.50BA+PC+1.5CC	PC	0.50	CC	1.5
0.50BA+PC+1.0SA	PC	0.50	SA	1.0	0.75BA+PC+1.5CC	PC	0.75	CC	1.5
0.75BA+PC+1.0SA	PC	0.75	SA	1.0	1.00BA+PC+1.5CC	PC	1.00	CC	1.5
1.00BA+PC+1.0SA	PC	1.00	SA	1.0	0.25BA+PC+2.0CC	PC	0.25	CC	2.0
0.25BA+PC+1.5SA	PC	0.25	SA	1.5	0.50BA+PC+2.0CC	PC	0.50	CC	2.0
0.50BA+PC+1.5SA	PC	0.50	SA	1.5	0.75BA+PC+2.0CC	PC	0.75	CC	2.0

The constant mixture parameters for all specimens

Cement: 450 g	Sand: 1350 g	Water: 225 g	w/c : 0.5
CEM — cement type,	BA — boric acid,		
AC — accelerator type,	PC — ordinary Portland cement,		
BAB — active belite cement,	CA — calcium aluminate cement,		
N — none,	SA — sodium aluminate,		
CC — calcium chloride.			

pH value and electrical conductivity (EC) of pore water are related to total anion and cation quantity in the process of hydration of cement compounds. As the amount of water-soluble salts increases, EC increases. Basic components forming PC such as tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) react with water and form the hydration products. During hydration, amounts of cation such as Ca^{++} , Mg^{++} , Na^+ , K^+ and $(OH)^-$ anion increase depending upon cement type, fineness, pH value of environment and temperature (T) of the environment in pore water compared to mixing water. So pH, T and EC values measured in cement paste increases quickly with the contact of cement with water. However pH, T and EC values of the environment are expected to decrease in case of presence of substances which can be water-soluble and form compound with anions or cations in the environment. Taking into account above consideration, firstly, mortars were prepared by CAC, the BAB and AC added PC, then the affect of B_2O_3 concentration on T , pH and EC values of these specimens were analyzed in detail.

3. Result and discussion

When 2 mol $B(OH)_3$ are heated about $600^\circ C$ ($2B(OH)_3 + \text{heat} \rightarrow B_2O_3 + 3H_2O$) it forms 1 mol B_2O_3

and 3 mol water. When 1 g $B(OH)_3$ is heated, approximately 0.577 g B_2O_3 is obtained. B_2O_3 ratios corresponding stoichiometrically to 4 different ratios of $B(OH)_3$ used in cement specimens are calculated with the relation given in Eq. (1):

$$M_{B_2O_3} = c \times 0.02 \times 0.577. \quad (1)$$

Here $M_{B_2O_3}$ is the amount of B_2O_3 included in mortar mixture and c is cement dosage. The B_2O_3 ratio of BAB cement is calculated as the 1.12% of cement weight. Changes in IST and FST of cement specimens according to B_2O_3/c ratio are given in Figs. 1–3. According to this:

- When compared to the control mortars with PC, the more B_2O_3/c ratio increases, the more IST of the mortar with PC increases significantly. The IST and FST of mortars at ratio of $B_2O_3/c > 0.06\%$ exceeded the values of BAB cement. When compared to control mortars with PC and BAB, the IST and FST of control mortars with CAC are much longer. However CAC specimens including BA at B_2O_3/c ratio of 0.17–0.18, this time reaches maximum, but it decreases at the ratio of $B_2O_3/c > 0.2$.
- ST of the mortar including 1% SA and BA is closer to the PC mortar, but it is shorter than the BAB mortar. SA ratio increases, IST and FST

decrease for all B_2O_3/c ratios. But this decrease of the ST enables workability. This situation shows difference in the PC mortar which was added CC. Both CC and B_2O_3/c ratios significantly affect STs. The IST and FST in the specimens added 1% CC increase up to the ratio of $B_2O_3/c < 0.07$. Even in these ratios STs of BAB mortar are exceeded. On the contrary, the STs of mortars prominently reduced at $B_2O_3/c > 0.07$ the ratios. The STs reduced rapidly on higher CC ratios. However, the workability gets harder at $B_2O_3/c > 0.17$ for the 1.5% CC ratio and $B_2O_3/c > 0.1$ for the 2.0% CC ratio.

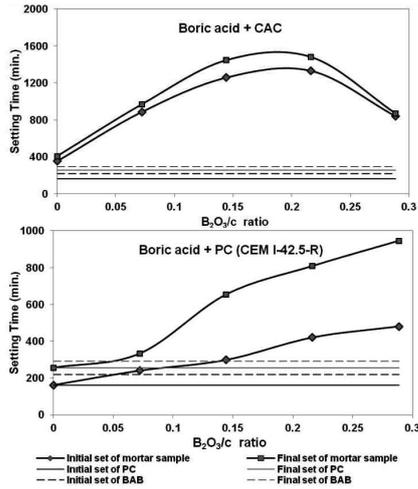


Fig. 1. Changes of IST and FST of PC and CAC mortar including BA according to B_2O_3/c ratio.

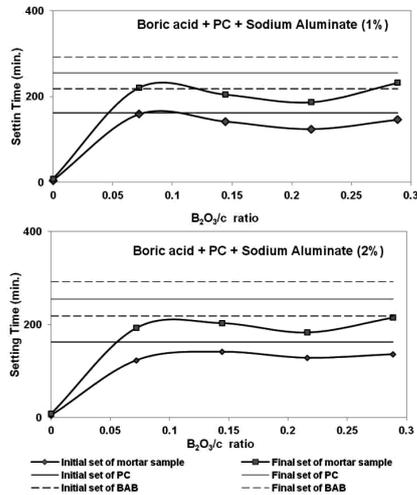


Fig. 2. Changes of IST and FST of PC mortar added 1% and 2.0% SA and BA depending upon B_2O_3/c ratio.

Besides T -pH-EC values depending on the time of mortars are measured with pH-EC meter device and the obtained findings were given in Figs. 4–12. According to graphics, the effect of BA on HT changes in the mortar specimens with chemical additive or not were determined as follows.

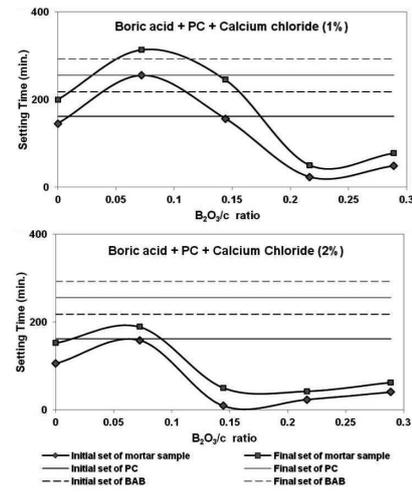


Fig. 3. Changes of IST and FST of PC mortar added 1% and 2.0% CC and BA depending upon B_2O_3/c ratio.

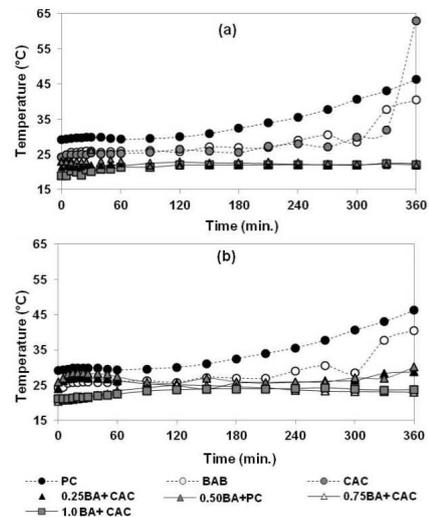


Fig. 4. Time-dependent T changes of the mortar specimens of pure CAC, CAC (a) and PC (b) including different ratios of BA and also control (pure PC and BAB).

While T of components were $\approx 20^\circ\text{C}$ prior to the mix, when the PC from control specimens contacted with water, the average T of mixture increased to 29°C and after 6 h it reached 46°C . The T of BAB mortar which is another control specimen increased to $\approx 24^\circ\text{C}$ immediately after contacting water and after 6 h it reached approximately 40°C . On the contrary, while the T of CAC mortar was $\approx 24^\circ\text{C}$ after contacting water, after 6 h it exceeded approximately 63°C . The HT of CAC specimens which was added BA at 0.25–0.50–0.75 and 1.0% ratios by weight of cement remained about $\approx 22^\circ\text{C}$. This situation shows that the hydration of CAC cement was completely stopped by the ratio of 1% BA at the 6 h period. The HT of PC mortars including 0.25–0.5% BA close to BAB specimens. On the other hand, the T of PC specimens with 0.75–1% BA were around $\approx 24^\circ\text{C}$ during the same period. It also shows that BA significantly retard the hydration of PC, though not as much as CAC (Fig. 4).

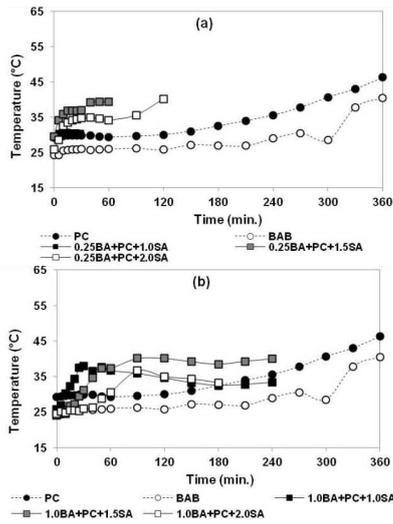


Fig. 5. Time-dependent T changes of PC mortar specimens which were added 0.25% BA (a) and 1.0% BA (b) as well as at the different rates of SA and also control mortars.

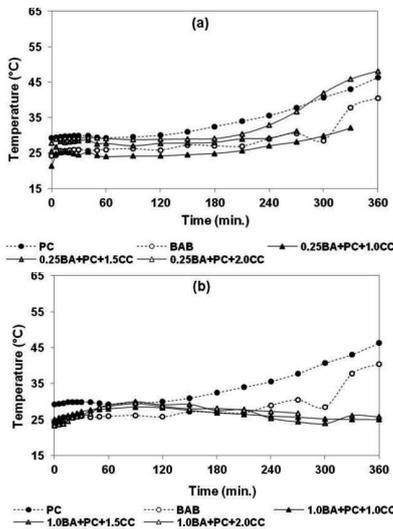


Fig. 6. Time-dependent T changes of PC mortar specimens which were added 0.25% BA (a) and 1.0% BA (b) as well as at the different rates of CC and also control mortars.

The T changes related to time of specimens added SA and BA free could not be measured because of very rapid setting of specimens (< 10 min). On the contrary, the HTs of specimens with SA and 0.25% BA increased as related to increase of SA ratio (for 1.5–2% SA) and it reached approximately 40°C after 6 h. While the HT of mortars with SA did not change too much together with increases of BA ratio, the STs of specimens extended. In addition, the HT of mortar with 1% BA decreased to the level of PC specimens, while the HT of mortars including BA at rates of 0.25–0.50–0.75% were too much from the values of PC specimens (Fig. 5). The HTs of mortars with 1–1.5% CC and not including BA generally were between PC and BAB (control) specimens and

the HTs of specimens with 2% CC reached $\approx 57^\circ\text{C}$ after 6 h. While the HTs of specimens including 0.25% BA and 2% CC similarly exceeded $\approx 48^\circ\text{C}$ after 6 h, the HTs of other specimens remained below the values of BAB specimens (Fig. 6).

The effect of BA to pH changes of porous water in mortar specimens with or without accelerator additive was explained in below according to Figs. 7, 8 and 9:

- At the beginning of hydration, the concentrations of free Ca^{++} , Mg^{++} , Na^+ and K^+ cations and $(\text{OH})^-$ anions dissolved from the cement compounds are high. The cement paste formed from hydrate gels begins to solidify, the concentration of alkaline ions in porous water slightly reduces. pH value of cement paste is an important indicator in terms of speed and continuity of hydration, even if not about strength.
- While pH value of control PC specimen was about 13.0 at the beginning, it regressed to 12.4 after 6 h. pH value of BAB specimens was also about 13.0 at the beginning, it decreased gradually until value of 12 in 300 min, and then it reached rapidly value of 12.8 after 6 h. This situation can be correlated to the forming CBH_6 compound as dissolving of BCs in chemical structure of BAB cement ($\approx 1.12\%$ B_2O_3) in alkaline medium, it precipitates on the surfaces of cement particles and CBH_6 compound dissolution due to lack of enough alkaline ions in the pore water, so beginning of hydration again. While pH value of CAC specimen without BA was value of 11.8 at the beginning, it decreased to value of 9.4 at the end of 330 min and at the end of 6 h it reached to value of 11.4 again. These values are significantly lower both from the values of the PC and BAB specimens. This situation is specific to the presence of about $\frac{1}{2}$ ratio of CaO in the chemical structure of CAC clinker compared to the PC clinker. pH value in CAC specimens with BA decreased approximately to values of 8–9 depending upon the increasing BA ratio. This situation indicates that BCs retard to the ST of CAC cement is much longer compared to the PC. In the PC specimens including BA, pH values decreased at a 270 min period depending upon the BA ratio compared to the control PC specimens and it reached to the same ratio again at the end of 6 h period. However the pH values of all specimens in this group were much higher than BAB specimens at the end of 330 min period (Fig. 7).
- The pH values in all of specimens with SA and BA at 0.25% ratio were lower than both the PC and BAB specimens. However this situation may be related to the very rapid setting. The more SA ratio increased, the more pH value decreased to a value of about 10 depending on the speed

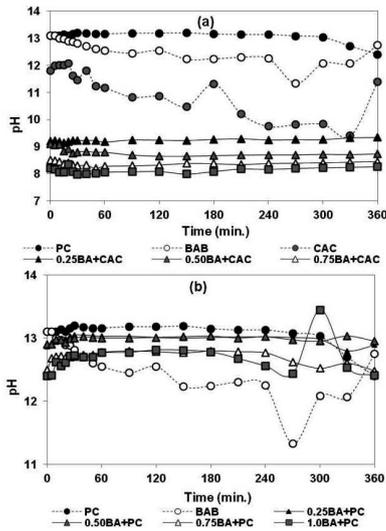


Fig. 7. Time-dependent pH changes of pure CAC, different ratios of BA including CAC (a) and PC (b) and control mortar mixtures.

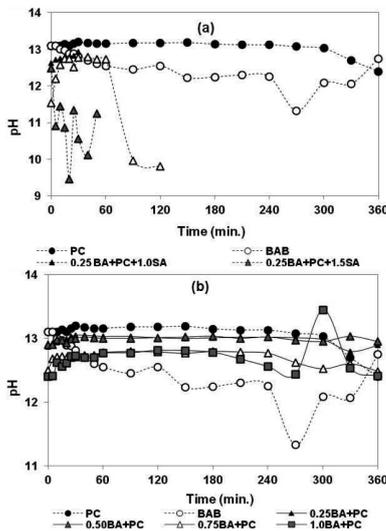


Fig. 8. Time-dependent pH changes of PC mortar specimens which were added 0.25% BA (a) and 1.0% BA (b) as well as at the different rates of SA and also control mortars.

of cement paste setting. In the specimens with SA and BA at 0.50%, while the pH values were the range of pH values of PC and BAB specimens for the 30–120 min period, it decreased to a value of 9.4 depending on solidifying in about 150 min. While the pH values of specimens with 1–2% SA and 0.75% BA were the range of pH values of PC and BAB specimens for the 30–180 min period, the pH value of the specimen with 2% SA fluctuated in the range of 12.8–10.5 in 60–180 min period and then the specimen solidified the pH value of 10.8. Initially, while the pH values of specimens with SA and 1% BA had a pH value of about 11.5, it reached to the value of 12.6–13.0 in the 30–240 min (Fig. 8).

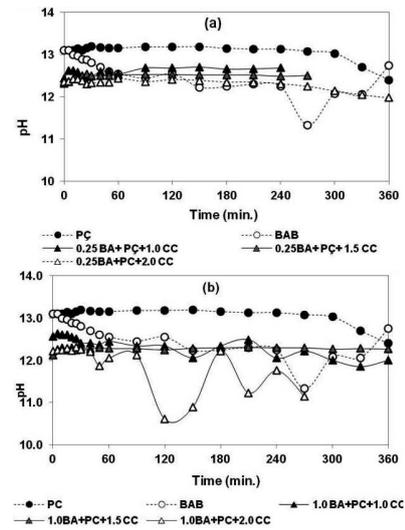


Fig. 9. Time-dependent pH changes of PC mortar specimens which were added 0.25% BA (a) and 1.0% BA (b) as well as at the different rates of CC and also control mortars.

- The pH values of specimens with CC and without BA were the range of pH values of PC and BAB specimens, and the more CC ratio increased the more pH value of these specimens approached to BAB specimens. A similar situation was true for the specimens with CC and 0.25–0.50% BA, as the BA ratio increased the ST gets longer. The specimen with 0.75 BA and 1.5% CC did not comply with this situation. In this specimen, the fluctuation of pH values between 12.4 and 10.1 was a clear indicator of the continued intermittent of hydration. In the 6 h period, while the pH values of specimens with 1% BA and 1.0–1.5% CC were closer to BAB, the pH value of specimens with 2% CC varies between 10.6 and 12.3, and the specimen solidified in the end of 270 min (Fig. 9).

By analyzing Figs. 10, 11, and 12, the effect of BA to the EC changes in pore water of specimens with or without chemical additive was explained below.

- At the beginning of hydration, while the EC value of control PC specimen was 18.7×10^3 mS/cm, it reached maximal value (26.3×10^3 mS/cm) in about 270 min. EC value rapidly increased and reached 14.5×10^3 mS/cm at 150–180 min period. It nearly showed a linear decrease and regressed to 10.3×10^3 mS/cm at 180–330 min period and then reached to 17.1×10^3 mS/cm at 330–360 min period. At the same time, this period of time is the FST for PC cement. EC value decreased to 4.4×10^3 mS/cm between 270–360 min. In term of EC value, BAB-control specimen was different from the PC-control specimen. At the beginning of hydration, while the EC value was 8.6×10^3 mS/cm, this value reached the value of 9.6×10^3 mS/cm in the first 10 min and then it decreased to a value of 3.0×10^3 mS/cm

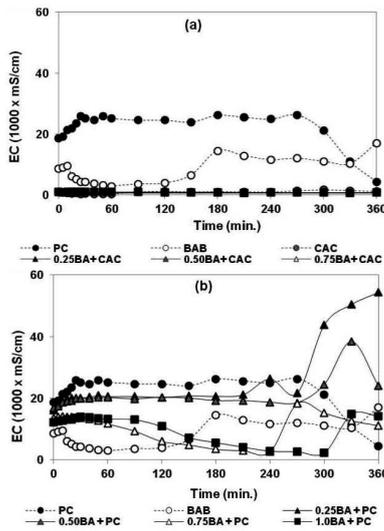


Fig. 10. Time-dependent EC changes of additive free and different ratios of BA including CAC (a) and PC (b) and control mortar mixtures.

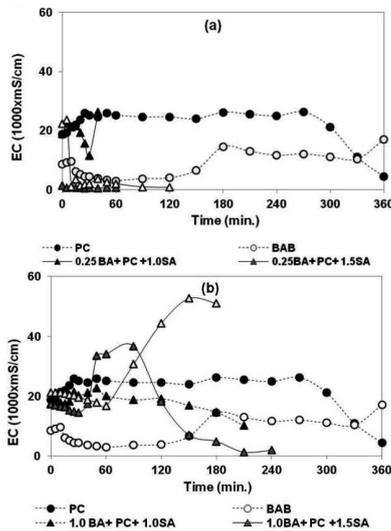


Fig. 11. Time-dependent EC changes of 0.25% (a) and 1.0% (b) ratios of BA, different ratios of SA included PC and control mortar mixtures.

in the next 40 min. In this period, it is thought that $B[OH]_4$ dissolved in pore water reacted with anions and cations and formed CBH_6 (or N_2BH_6 and K_2BH_6) then precipitated on cement particles and retarded hydration. In 150–180 min period, EC values increased rapidly and reached the value of 14.5×10^3 mS/cm. In 180–330 min period, it showed a linear decrease and regressed to the value of 10.3×10^3 mS/cm. Then it reached a relatively high value as 17.1×10^3 mS/cm in 150–180 min period. Reducing of the EC values at longer period shows that the formation of CBH_6 compounds and these formations covered on the cement particles in a long time. On the contrary, the rapid increase of EC value in a short time indicated that CBH_6 dissolves rapidly as related to the excessive

decrease of alkalinity in medium. Precipitation and dissolution cycles continue during hydration period until consuming of ions in the medium (Fig. 10).

- In PC specimen with BA, the more increasing BA ratio, the more decreasing EC values. In the specimens with 0.25% BA, while EC values were $\approx 20 \times 10^3$ mS/cm at 40 min, it rapidly reached to 54.4×10^3 mS/cm in next period. For the specimens with 0.5% BA, firstly the EC value reached 38.5×10^3 mS/cm in end of the 330 min and it regressed to 24×10^3 mS/cm between 330 and 360 min. The EC values of specimens with 0.75% and 1.0% ratio BA represent fluctuations such as 13–2.7–18–11.2 $\times 10^3$ mS/cm and 12.1–14–2.3–14.9 $\times 10^3$ mS/cm, respectively. This situation clearly shows precipitation and dissolution cycles of borate compounds. The EC values of CAC specimens with BA and without BA are very low. The EC values of fresh specimens with 0.25% BA and 1% SA are about 18.9–22.5–11.5 and 26.3×10^3 mS/cm in the first 40 min of hydration and these specimens solidified. Solidification of specimens with 1.5% SA rapidly occurred. ST of specimens with 2% SA is about 10 min. The same condition is current for specimens with 0.50% SA. ST of this specimens increases a little and it reaches average to 30 min. Due to rapid solidification of both specimens these have not workability and applicability for traditional concrete. The EC values of fresh specimens with 0.75% BA and 1% SA are about 17.8–19.8–11.8–16.1 and 10.6×10^3 mS/cm in the first 180 min of hydration and these specimens solidified. Solidification of specimens with 1.5% SA occurred in 30–40 min. EC values of specimens with 2% SA increased from 21.4×10^3 to 41.9×10^3 mS/cm during 90 min and regressed to 17.6×10^3 mS/cm in next 60 min. FST of specimens with 2% SA is approximately 150 min. The same condition is current for specimens with SA and 1% BA. Especially, EC value of specimens with 2% SA reached to 52.7×10^3 mS/cm at the end of 150 min and FST of the specimen is about 180 min (Fig. 11).

- When EC values of specimens with CC and without BA was analyzed, it reached to 56.5×10^3 mS/cm at the end of 300 min for 1% CC, 55.6×10^3 mS/cm at the end of 240 min for 1.5% CC and 52.7×10^3 mS/cm at the end of 270 min for 2% CC. EC values of specimens with 0.25% BA also reached to 37×10^3 mS/cm at the end of 330 min for 1% CC, 37.3×10^3 mS/cm at the end of 180 min for 1.5% CC, 30×10^3 mS/cm at the end of 150 min for 2% CC and 83.7×10^3 mS/cm at the end of 330 min for 2% CC. The EC values of specimens with 0.50% BA are close to those of control specimens (PC). While BA ratio of specimens was increasing, EC values quickly decreased (Fig. 12).

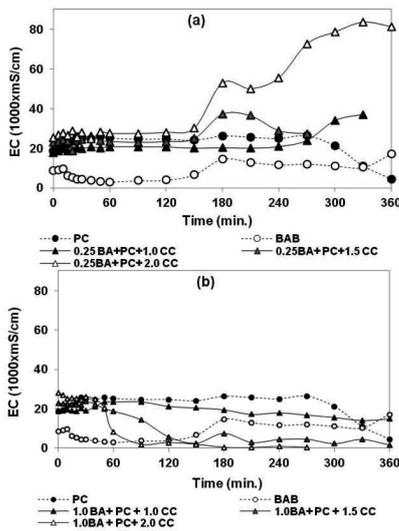


Fig. 12. Time-dependent EC changes of 0.25% (a) and 1.0% (b) ratios of BA, different ratios of CC included PC and control mortar mixtures.

4. Conclusion

This study is aimed at obtaining of the mortar mixture designs having the highest possible B_2O_3/c ratio and the closest penetrability and hydration properties to control mortar mixtures. So setting retardation and strength problems will be resolved and the expected technological benefit can be obtained.

In the study four different B_2O_3/c ratios (0.07, 0.15, 0.22, and 0.30) are used. Two different chemical substances are tested as stabilizers in order to suppress the effect of setting retardation of BA. At first, IST and FST are calculated. IST and FST of control mortar mixtures are 162–255 min for PC, 218–292 min for BAB and 353–407 min for CAC. The IST and FST of CAC specimens including BA increased 2–4 times. In stabilizer-free PC specimens for the rate of $B_2O_3/c = 0.3$, IST increased twice and the FST increased 3 times. In mortar mixtures including stabilizers for the rate of $B_2O_3/c = 0.3$, IST and FST of mortar mixtures with CC are 40 min and 80 min, respectively. IST and FST of mortar mixtures with SA are about 140–240 min. In CAC specimens because of anion and cation insufficiency in the environment, the formation of CBH_6 , precipitation onto cement particles and dissolve again circulation occur in a long process. So compared to the STs of PC, BCs is much more in retard than the STs of CAC.

T is an indicator of hydration speed. In 6 h periods, T reached to 46°C in PC specimen and 40°C in BAB specimens according to time-dependent T data. For $B_2O_3/c = 0.3$ ratio, the T values is about 27°C in specimen with CC and between 33 and 40°C in specimens with SA.

Higher or lower pH values can be related to the reaction of cement particles with pore water or the deceleration of the hydration reaction. pH value of control PC specimens is about 13 after contact with water, in during

substantially whole of the 6 h period it continued in the same manner. Initially, while pH value of BAB specimen was 13, it decreased gradually and it regressed to 11 at 4 h and then again it reached to 12.8. This situation is related to CBH_6 formation. For the ratio of $B_2O_3/c = 0.3$, pH value of specimen with SA only reached to 13 among the specimens used stabilizer.

EC value is also important in terms of showing the total ion content in porous water and thus the solubility of cementitious compounds. The EC value of control PC specimen is 26000 mS/cm between 4 to 5 h. In BAB specimens it was 9000 mS/cm at first and then regressed to a value of 3000 mS/cm, increased 12000 mS/cm in 4–5 h period and reached 17000 mS/cm in the end of 6 h period. For the $B_2O_3/c = 0.3$ ratio, while EC value of specimen with SA reached to 52000 mS/cm in the end of 150 min, the EC value of specimen with CC was 28000 mS/cm at the first, then it rapidly regressed to 2000 mS/cm in the end of 90 min.

As a result, for the highest B_2O_3/c ratio (0.3) chosen in this study, the closest properties to the workability and other properties of control-PC specimens was provided by SA accelerator considering the IST and FST, T , pH, and EC values.

Acknowledgments

This study was supported by the Suleyman Demirel University Scientific Research Project Coordination Unit (Project No. 2573M10).

References

- [1] S. Bell, P.V. Coveney, *Molecular Simulation*, Informa, UK 1998, p. 331.
- [2] I. Kula, A. Olgun, V. Sevinc, Y. Erdogan, *Cem. Concr. Res.* **32**, 227 (2002).
- [3] Ş. Targan, A. Olgun, Y. Erdoğan, V. Sevinç, *Cem. Concr. Res.* **33**, 1175 (2003).
- [4] A. Sağlık, O. Sümer, E. Tunç, M.F. Kocabeyler, R.S. Çelik, *DSI technical bulletin*, Vol. 105, Ankara 2009.
- [5] D.E. Volkman, P.L. Bussolini, *JTE* **20**, (1992).
- [6] D. Demir, G. Keleş, *Nucl. Instrum. Methods Phys. Res. B* **245**, 501 (2006).
- [7] BOREN, “Bor ve çimento”, http://www.eie.gov.tr/duyurular/EV/EV_etkinlik/2008_bildiriler/04-OTURUM_ve_AR-GE/0403.pdf.
- [8] H.F.W. Taylor, *Cement Chemistry*, 2nd ed., Thomas Telford Pub., London 1997.
- [9] J.R. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York 1990.
- [10] J. Jeffrey, L. Garner, W. House, *Waste Manag.* **2**, 359 (1991).
- [11] *Analyses Results of Monthly (November) BAB Cement in GOLTAS Cement Co. Operation*, Isparta 2007.
- [12] *Analyses Results of Monthly Cement in GOLTAS Cement Co. Operation*, Isparta 2009.
- [13] TS EN 196-3, *Methods of testing cement-part 3: Determination of setting time and soundness*, Turkish Standard Institute TSE, Ankara 2003.